A critical investigation of the effect of hygrothermal cycling on hydration and in-plane/through-plane proton conductivity of Nafion 117 at medium temperature (70–130 °C)

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HIGHLIGHTS

► Proton conductivity of Nafion 117 from 70 to 130 °C under controlled relative humidity.
► Membrane hydration under the environmental conditions of conductivity measurements.
► Effect of temperature and relative humidity cycling on hydration and through-plane/in-plane conductivity.
► Determination of activation energy for conduction at constant hydration.

ARTICLE INFO

ABSTRACT

Hydration, in-plane and through-plane conductivity of Nafion 117 membranes are investigated in the temperature range 70–130 °C and in the relative humidity (RH) range 50–90% upon cycling RH, at constant temperature, and cycling temperature at constant RH. Both temperature and RH cycling result in hysteresis of conductivity and hydration. During the RH cycle, conductivity changes at decreasing RH are faster than hydration changes, thus indicating the presence of water molecules contributing weakly to conductivity. During the temperature cycle, the in-plane conductivity shows a hysteresis loop where, as expected, the more hydrated state is the more conductive state as well. However, under the same conditions of temperature and RH, the through-plane conductivity exhibits an anomalous behaviour where the lower conductivity is associated with the higher hydration level. Upon temperature cycling, through-plane and in-plane conductivity show different temperature dependence during heating but the same dependence during cooling. This behaviour is attributed to irreversible structural changes occurring during heating when the membrane is pressed between the electrodes in the through-plane conductivity cell. The possible influence of the through-plane conductivity hysteresis on the performance of a PEM fuel cell in the range 70–130 °C is also discussed.

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1. Introduction

Perfluorosulfonic acid membranes, and among them mostly Nafion membranes, are currently used as solid polymeric electrolytes in fuel cells (PEMFCs) [1–8] due to their outstanding properties in terms of high chemical inertness, good thermal stability and excellent proton conductivity when highly hydrated.

PEMFCs are operated in the temperature range 50–90 °C, but working temperatures above 90 °C are desirable since they would simplify the PEMFC cooling system, promote the reactions at the electrodes and allow feeding the PEMFC with hydrogen containing CO impurities.

Understanding to what extent the polymer electrolyte limits fuel cell operation at temperatures above 90 °C needs the investigation of membrane properties, such as conductivity and hydration, at those temperatures. While several papers deal with membrane conductivity above 90 °C [9–37], there is only a limited number of papers reporting membrane hydration above 90 °C at the environmental conditions under which the conductivity data were collected [32–37]. The knowledge of hydration is however of fundamental importance, since the water content is responsible for different membrane properties including proton conductivity, swelling and mechanical stability.

In a recent paper [32] we described a simple gravimetric method allowing the determination of water uptake up to 140 °C

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even at relative humidity (RH) close to 100%. This method was used to investigate the relation between the conductivity and the hydration of sulfonated polyethersulfone membranes in the temperatures range 70–120 °C. It was also shown that cycling temperature and RH results in conductivity and hydration hysteresis so that the conductivity and the hydration at a certain temperature and RH value depend on the history of the changes the membrane underwent in terms of temperature and RH.

On the basis of the above results it was of interest to perform a similar investigation on Nafion 117 membranes. The present paper reports the effect of cycling RH at constant temperature and of cycling temperature at constant RH on the hydration and proton conductivity of Nafion 117. The determination of conductivity as a function of temperature at constant hydration allowed the calculation of the activation energy of conduction in the range 70–130 °C. Most conductivity measurements were performed by applying the electric field parallel to the membrane surface (in-plane conductivity), while a few measurements were carried out with the electric field perpendicular to the membrane surface (through-plane conductivity). The results obtained by through-plane and in-plane measurements are compared and discussed in terms of membrane structural changes occurring under the different measurement conditions.

2. Experimental

2.1. Chemicals

Nafion 117 membranes, 180 μm thick, were purchased from Ion Power (USA). Before use, all membranes were boiled in 3% (v/v) hydrogen peroxide, 1 M sulphuric acid and water, 1 h for each treatment. Sulphuric acid and hydrogen peroxide were supplied by Carlo Erba.

2.2. Techniques

The membrane through-plane conductivity was measured on Nafion 117 discs, 8 mm in diameter, sandwiched between gas diffusion electrodes (Pt free ELAT) which were pressed on the membrane by means of porous stainless steel discs; the initial applied pressure was 60 kg cm^{-2} and was not controlled during the experiment. Two-probe impedance measurements were carried out by a Solartron 1260 Impedance/Gain Phase Analyser in the frequency range 0.01 Hz–100 kHz at a signal amplitude ≤100 mV by using the cell described in ref.14. The impedance data were corrected for the contribution of the empty and short-circuited cell. The membrane resistance was obtained by extrapolating the impedance data to the real axis on the high frequency side.

The membrane in-plane conductivity was determined by four-probe impedance measurements in the frequency range 10 Hz–100 kHz using an Autolab, PGSTAT30 potentiostat/galvanostat equipped with an FRA module. The cell consists of two platinum foil electrodes (3 cm apart) to feed current, and two platinum wires (0.5 mm in diameter, 1 cm in length and 1 cm apart) to measure the potential drop across the membrane. The four electrodes are arranged on a Teflon disc. The Nafion membrane (5 cm × 0.5 cm) is pressed on the electrodes by a second Teflon disc where a rectangular window (0.8 cm × 1.3 cm) allows hydration and swelling of the membrane portion placed between the platinum wires (further details are reported in Ref. [14]).

In both in-plane and through-plane conductivity measurements, RH was controlled by using stainless steel sealed-off cells consisting of two communicating cylindrical compartments held at different temperatures. The cold compartment contained water, while the hot compartment housed the membrane under test. RH

values were calculated from the ratio between the pressures of saturated water vapour (p) at the temperatures of the cold (Tc) and hot (Th) compartment: RH = p(Tc)/p(Th) × 100.

Water uptake at controlled temperature and RH was determined by using the cell described in Ref. [32]. This cell has the same size and shape as the conductivity cell used for through-plane conductivity measurements and differs from that mainly because the MEA holder is replaced by a glass container hosting the membrane sample (≈0.5 g). The cell is equipped with a device which allows to close the sample container with a teflon plug without opening the cell. After a suitable equilibration time (usually a day) at the desired temperature and RH, the sample container is closed, extracted from the cell and weighed. The water content (λ, number of water molecules per sulfonic group) is determined on the basis of the weight of the polymer dried at 130 °C taking into account the amount of water trapped in the sample container at the temperature and RH of the experiment. The error on the determination of λ is estimated to be ±0.3 at most.

Water uptake determinations were also carried out for membranes kept under pressure between ELAT discs. More specifically 15 stacked membrane discs, 10 mm in diameter, were sandwiched between a couple of gas diffusion electrodes (Pt free ELAT) which were pressed on the membranes by means of porous stainless steel discs; the initial applied pressure was 60 kg cm^{-2} and was not controlled during the experiment.

According to Ref. [32], the error on the RH control is estimated to be lower than 2 RH units for both conductivity and water uptake cells.

Infrared spectra were recorded using a Bruker TENSOR27 spectrometer equipped with a Deuterium Triglycine Sulphate (DTGS) detector. ATR spectra were collected with a Gateway ATR accessory from SPECAC, using a six reflection horizontal ATR sampling system equipped with a ZnSe crystal. The sample was placed on top of the ZnSe crystal at room temperature and each ATR spectrum was the average of fifty scans, measured with a resolution of 2 cm^{-1} in the 400–4000 cm^{-1} range.

3. Results and discussion

3.1. Conductivity and hydration at 70 °C

The in-plane conductivity of Nafion 117 was initially investigated as a function of RH at 70 °C. A first set of measurements was carried out at increasing RH from 50 to 90% with steps of 10 RH units. The conductivity increased with RH ranging from 0.035 S cm^{-1} to 0.12 S cm^{-1}. At the end of the measurements RH was decreased to 50% and, after one day equilibration, a second set of measurement was started again. Fig. 1 shows that the logarithm of conductivity depends linearly on RH and that the conductivity changes reversibly with RH.

The water uptake (λ) of a Nafion sample was also determined at 70 °C as a function of RH: λ values range from 5.2 to 9.5 with RH increasing from 50% to 90%, respectively (Fig. 2). Subsequently, the same Nafion sample was conditioned for one day at 70 °C − 50% RH and the water content was determined again: the λ value was 7.0, significantly higher than that found at the beginning of the experiment at the same RH value. This was surprising because, under the same conditions of temperature, RH and equilibration time, the conductivity of the second set of measurements turned out to be coincident with that of the first set, within measurement errors (Fig. 1). Further RH increase to 90% gave the same λ value measured at the end of the first set of measurements.

These results suggested to further investigate the long term evolution of both hydration and in-plane conductivity after decreasing RH from 90% to 50%. To this aim two Nafion samples,
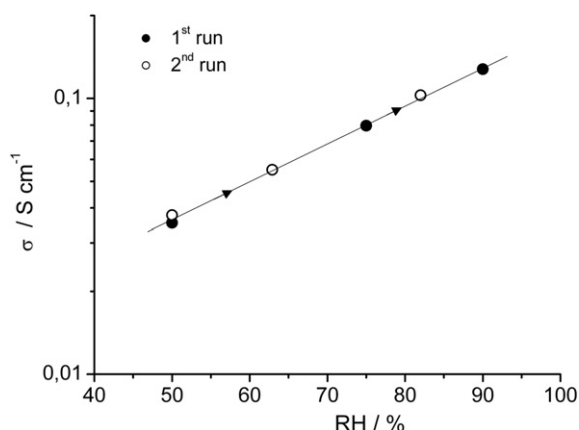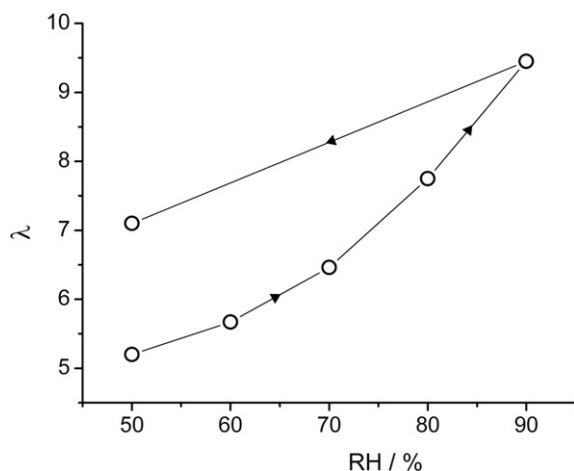
Fig. 1. In-plane conductivity (σ) of Nafion 117 at 70 °C as a function of RH. Measurements were carried out at increasing RH; the second run started one day after the end of the first run.

Fig. 3. Time dependence of in-plane conductivity (σ) and water content (λ) at 70 °C and 50% RH for Nafion 117 samples that were previously equilibrated at 70 °C and 90% RH.
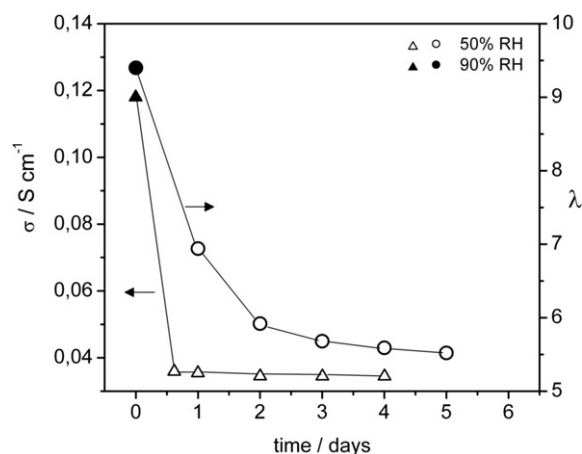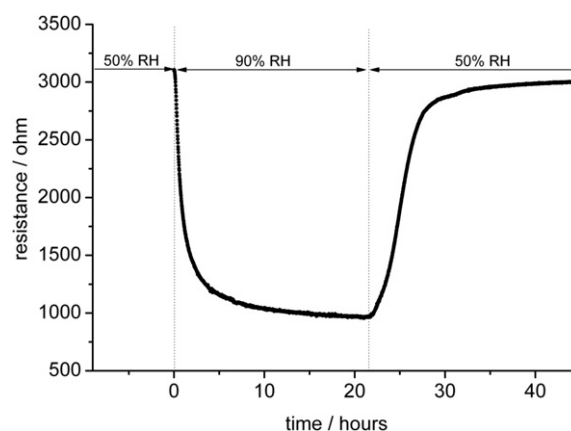
one in the water uptake cell and the other in the conductivity cell, were conditioned at 90% RH for one day. RH was then decreased to 50%, and conductivity and hydration were determined as a function of time (Fig. 3). While the conductivity measured after 15 h was by only 4% higher the final conductivity, the membrane hydration decreased slowly and in five days approached the value ($\lambda = 5.2$) reported in Fig. 2 at the beginning of the RH cycle.

Similar results, in terms of different time evolution of hydration and conductivity, were obtained for the through-plane conductivity and the hydration of Nafion 117 samples that were sandwiched between Pt-free ELAT discs with a pressure of 60 kg cm^{-2}. As previously described, the membranes underwent the RH cycle 50% → 90% → 50% at 70 °C with equilibration time of one day at each RH value for both conductivity and water uptake determinations. While reproducible conductivity values were measured at the beginning and at the end of the RH cycle, a $\Delta\lambda$ of 2.5 was found between the final and the initial λ value. These results confirm those previously reported for in-plane conductivity measurements, indicating that the conductivity response to the decrease in RH is much faster than the corresponding hydration response independent of how (in-plane or through-plane) conductivity is measured.

On the other hand, one could speculate that the different time dependence of conductivity and hydration on RH changes may simply arise from a different kinetics of water loss in the conductivity and water uptake cells. In order to prove unambiguously that

this is not the case, in-plane conductivity measurements were carried out by placing a Nafion membrane inside the water uptake cell.

After membrane conditioning at 70 °C − 50% RH for one day, RH was changed according to the sequence 50% → 90% → 50%, allowing the membrane to equilibrate at each RH value for one day, as in the case of water content determinations. Fig. 4 shows the membrane resistance as a function of time during the RH cycle. It can be observed that the final resistance value is lower by only 3% than the resistance value at the beginning of the experiment, while according to Fig. 2 the final water content ($\lambda = 7.0$) is still far from the initial water content of the membrane ($\lambda = 5.2$).

On the basis of these results it can be concluded that water content and conductivity of Nafion 117 exhibit different time dependence during dehydration, which seems to indicate the presence of water molecules, strongly bonded to the ionomer, that are slowly lost and do not contribute significantly to the membrane conductivity. This suggestion is supported by recent results of combined proton conductivity and time-resolved ATR-FTIR measurements during hydration/dehydration cycles at room temperature [38]. It was shown that the initial increase in hydration of a dry Nafion NRE211 membrane is characterised by a $\delta(HOH)$ band around 1740 cm^{-1} and is not accompanied by a significant increase in proton conductivity. However, further hydration gives rise to a

Fig. 2. Water uptake (λ) of Nafion 117 at 70 °C as a function of RH. Arrows indicate the direction of RH changes.

Fig. 4. In-plane resistance, at 70 °C, as a function of time during the RH cycle 50% → 90% → 50% for a Nafion 117 sample located inside the water uptake cell.
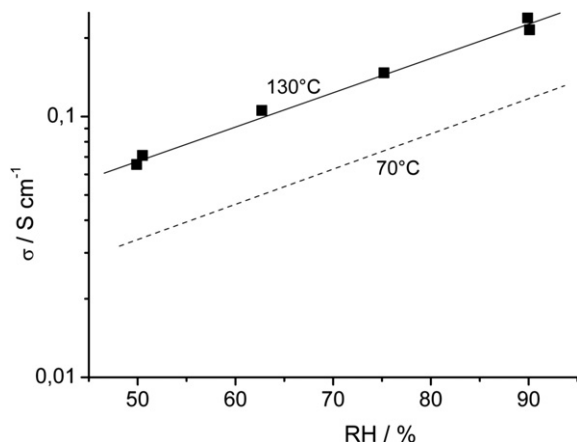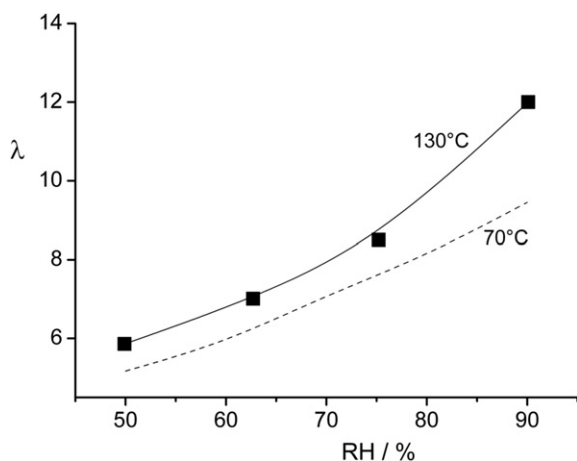
Fig. 5. In-plane conductivity (σ) of Nafion 117 at 130 °C as a function of RH. Measurements were carried out at increasing RH. The conductivity at 70 °C is reported for comparison.

rapid conductivity increase in proportion to the intensity of a new δ(HOH) band around 1630 cm^{-1}. Upon dehydration, after a rapid conductivity decrease, and the concomitant decrease in the intensity of the band at 1630 cm^{-1}, the dehydration proceeds very slowly without significant loss of proton conductivity. This is actually what is observed in Fig. 3 for the time dependence of water content and conductivity of Nafion 117 at 70 °C.

3.2. Conductivity and hydration at 130 °C

A second set of in-plane conductivity measurements were carried out at 130 °C as a function of RH on a sample previously conditioned overnight at 130 °C − 50% RH in the conductivity cell. As already observed at 70 °C, the logarithm of conductivity depends linearly on RH (Fig. 5) and the conductivity increases from 0.06 S cm^{-1} to 0.21 S cm^{-1} in the RH range 50−90%.

Water uptake at 130 °C was also determined as a function of RH: λ increases from 6.3 at RH = 50% up to 12.0 at RH = 90% (Fig. 6). In agreement with the literature [39], comparison of λ values obtained at 70 and 130 °C shows that the increase in temperature at constant RH results in an increase in λ such that the higher the RH, the larger the λ changes. On the other hand, the hydration of a sample that was previously heated to 130 °C, at a given RH value, is maintained for at least one day when the sample is cooled to 70 °C at the same

Fig. 6. Water uptake (λ) of Nafion 117 at 130 °C as a function of RH. Measurements were carried out at increasing RH. The water uptake at 70 °C is reported for comparison.

RH (Table 1). This is consistent with the results reported for Nafion 117 in contact with liquid water at different temperatures [40] showing that the equilibrium hydration attained at a given temperature tends to be maintained at lower temperatures.

The relation between conductivity and hydration at 70 and 130 °C is displayed in Fig. 7 where the solid symbols refer to data collected at increasing RH, while the open circle represents the σ/λ values at 70 °C for a sample that was cooled from 130 to 70 °C at RH = 90%. It can be seen that the two curves of log σ versus λ are nearly parallel, thus indicating that the conductivity change with temperature at constant hydration is substantially independent of λ. As a consequence the activation energy of conduction as well is expected to be weakly dependant on water content for λ values in the range 6−12.

3.3. Temperature dependence of in-plane conductivity at constant λ

On the basis of the data displayed in Fig. 6 it can be inferred that the increase in conductivity with temperature at constant RH must reflect the increase in both temperature and hydration. Therefore, conductivity data collected under these conditions cannot be used to calculate the activation energy of proton transport. On the other hand, the data reported in Table 1 indicate that it is possible to keep the water content constant upon cooling the ionomer at constant RH.

Conductivity measurements were thus carried out at 50 and 90% RH with decreasing temperature in the range 130−70 °C in order to highlight only the temperature contribution to the conductivity and to calculate the activation energy of conduction. The dependence of conductivity on temperature for $\lambda = 6.3$ (RH = 50%) and 12.0 (RH = 90%) is displayed in Fig. 8 as Arrhenius plot (log(σT) versus $1/T$). The activation energy of conduction (E_a), calculated by the Arrhenius equation ($\sigma T = \sigma_0 \exp(-E_a/kT)$, where k is the Boltzmann constant), was 0.10 ± 0.02 eV for $\lambda = 12.0$ and 0.12 ± 0.02 eV for $\lambda = 6.3$. It is interesting to observe that, the water content being the same, the activation energy of conduction for aqueous solutions of sulphuric acid, calculated from literature data [41] in the temperature range 70−115 °C is very close to that of Nafion 117 (0.115 eV for $\lambda = 6.0$ and 0.106 eV for $\lambda = 12.0$).

3.4. Temperature dependence of through-plane conductivity at constant RH

In a previous paper [11] it was reported that, for RH < 75%, the through-plane conductivity of Nafion 117 membranes is nearly independent of temperature when the membranes are heated for the first time in the temperature range 80−140 °C at constant RH. On subsequent cooling, the conductivity is lower than that of the heating run and the difference in conductivity increases as temperature decreases. This is just the opposite of that observed for the in-plane conductivity of Nafion 117 whose temperature dependence during the first heating run is stronger than that observed during the subsequent cooling due to the irreversible increase in the membrane hydration. As an example, Fig. 9 shows the temperature dependence of the in-plane conductivity upon heating − cooling at 90% RH.

Table 1
Water content (λ) of Nafion 117 before and after membrane cooling from 130 to 70 °C at constant RH.

| % RH	$\lambda \pm 0.3$ at 130 °C	$\lambda \pm 0.3$ at 70 °C
50	6.4	6.3
75	8.7	8.5
90	11.8	12.0
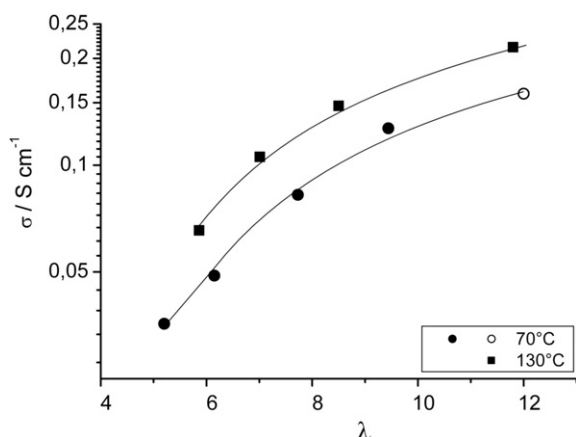
Fig. 7. In-plane conductivity (σ) as a function of water content (λ) for Nafion 117 at 70 and 130 °C. Solid symbols refer to data collected at increasing RH; the empty circle represents σ/λ values at 70 °C after cooling from 130 to 70 °C at 90% RH.

On the basis of these observations we redetermined the through-plane conductivity of a Nafion 117 membrane at RH = 70% during heating − cooling runs in the range 70–130 °C (Fig. 9). In agreement with Ref. [11] the change in conductivity upon heating (from 0.059 S cm^{-1} at 70 °C to 0.070 S cm^{-1} at 130 °C) turned out to be smaller than that observed upon cooling (from 0.070 S cm^{-1} at 130 °C to 0.048 S cm^{-1} at 70 °C). Interestingly, while upon heating the temperature dependence of through-plane and in-plane conductivities is clearly different (with apparent activation energies of 0.07 and 0.14 eV respectively), upon cooling the activation energy of the through-plane conductivity (0.11 ± 0.02 eV) is nearly the same as that calculated for the in-plane conductivity with a similar hydration level.

To ascertain whether the different temperature dependence of in-plane and through-plane conductivity arises from different changes in the membrane hydration, we determined the water uptake of membrane discs that were kept under the same pressure applied in the through-plane measurements (see Experimental section for details). During the thermal cycle 70 °C → 130 °C → 70 °C, at 70% RH, λ increased from 5.9 to 7.2 upon heating and kept nearly constant (7.4) after cooling. Since the hydration behaviour of the pressed membranes is similar to that of the free membranes, the different temperature dependence of through-plane and in-plane conductivity must be associated with irreversible structural changes, which
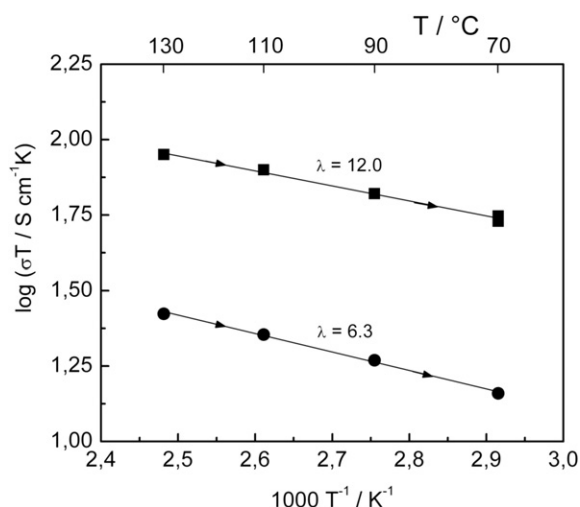
Fig. 8. Arrhenius plots for the in-plane conductivity of Nafion 117 samples with the indicated λ values. Arrows indicate the direction of temperature changes.
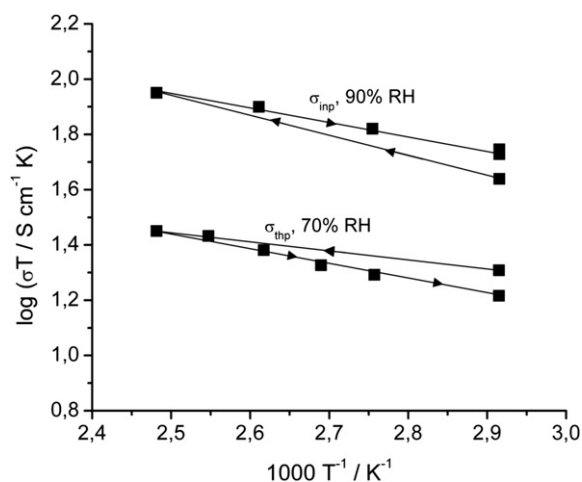

Fig. 9. Arrhenius plots for in-plane (σ_{inp}) and through-plane (σ_{thp}) conductivity of Nafion 117 at the indicated RH values during the temperature cycle 70 °C → 130 °C → 70 °C. Arrows indicate the direction of temperature changes.

occur when the membrane is heated under pressure and offset to some extent the increase in conductivity expected from the increase in temperature and hydration. In this connection one should take into account a) the type of swelling the membrane undergoes in the through-plane conductivity cell as well as b) the possible occurrence of condensation reactions between sulfonic groups leading to the formation of S−O−S bridges.

While in the cell for in-plane conductivity measurements the membrane is free to swell, in the cell for through-plane conductivity the membrane is constrained between the electrodes and forced to swell mainly in the direction parallel to them. According to Refs. [14,42] the resulting shear stress is expected to bring about a partial alignment of the conduction pathways along the swelling direction and the concomitant decrease in the through-plane conductivity.

As regards the occurrence of condensation reactions, the formation of S−O−S bridges can be revealed by FTIR spectroscopy since condensed sulfonic groups are characterised by an IR band at 1440–1460 cm^{-1} assigned to the elongation of the S=O bond [43,44]. To this aim FTIR spectra were collected for three samples including a) a membrane that underwent the temperature cycle 70 °C → 130 °C → 70 °C at 70% RH inside the through-plane conductivity cell, b) a membrane that underwent the same temperature cycle inside the in-plane conductivity cell and c) an untreated membrane. A weak band at 1454 cm^{-1} appeared only in the
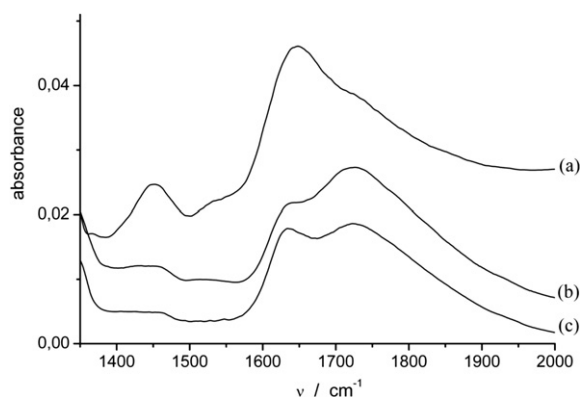
Fig. 10. ATR-FTIR spectra for membranes that underwent the temperature cycle 70 °C → 130 °C → 70 °C, at 70% RH, inside the through-plane conductivity cell (a) and inside the in-plane conductivity cell (b). The spectrum of an untreated membrane (c) is reported for comparison.

spectrum of the membrane treated inside the through-plane conductivity cell (Fig. 10) thus indicating that some condensation of the sulfonic groups, leading to a decrease in the proton concentration, takes place when the membrane is pressed between the electrodes.

The occurrence of both anisotropic swelling and condensation of sulfonic groups can therefore account for the weak temperature dependence of the through-plane conductivity upon heating.

Finally it can be observed that the factors responsible for the hydration and conductivity hysteresis (namely ionomer memory and condensation of sulfonic groups) occurring upon cycling temperature at constant RH are independent of membrane thickness. As consequence, conductivity and hydration hysteresis similar to that here reported for Nafion 117 membranes is also expected for the thinner PFSA membranes that are currently preferred to Nafion 117 in polymer electrolyte membrane fuel cells.

4. Conclusions

Hydration and conductivity of Nafion 117 were investigated in the temperature range 70–130 °C and in the RH range 50–90%. Cycling temperature and relative humidity gave rise to hydration and conductivity hysteresis which, in some cases, showed a substantially different dependence on both RH and temperature.

Hydration hysteresis is observed upon cycling RH at constant temperature and upon cycling temperature at constant RH. Surprisingly, the RH cycle does not result in conductivity hysteresis, thus suggesting the presence of water molecules which do not contribute to proton transport. On the other hand, the temperature cycle gives rise to an anomalous through-plane conductivity hysteresis where the lower conductivity is associated with the higher hydration level, due to irreversible modifications the membrane undergoes during heating. Only the in-plane conductivity shows a hysteresis loop where the more hydrated state is the more conductive state as well.

Conductivity changes upon temperature cycling are such that through-plane and in-plane conductivity show different temperature dependence during heating but the same dependence during cooling. The fact that the membrane hydration keeps constant upon cooling allowed the calculation of the activation energy of proton conduction.

All these results show the importance of the determination of hydration and conductivity under the same environmental conditions and the need of cycling temperature and RH for a better understanding of the factors underlying the conductivity changes.

As regards Nafion based fuel cells, the results obtained from cycling temperature at constant RH, in the absence and in the presence of an applied pressure, indicate that irreversible modifications of the membrane (anisotropic swelling and condensation of the sulfonic groups) take place when the membrane is heated under pressure. Such modifications are likely to occur when the Nafion membrane is pressed between the fuel cell electrodes as well, and are therefore expected to contribute to the loss of the fuel cell performance at medium temperature.

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